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<p>(21) International Application Number: <b>PCT/US97/23622</b></p> <p>(22) International Filing Date: <b>19 December 1997 (19.12.97)</b></p> <p>(71) Applicant (for all designated States except US): <b>THE PROCTER &amp; GAMBLE COMPANY [US/US]; One Procter &amp; Gamble Plaza, Cincinnati, OH 45202 (US).</b></p> <p>(72) Inventors; and  (75) Inventors/Applicants (for US only): <b>ONO, Masami [JP/JP]; 3-9-4-102, Sumiyoshihonomachi, Higashinada-ku, Kobe 658 (JP). BRYANT, Lonnie, Liddell, Jr. [US/JP]; La Mieux Momoyama 301, 87, Taichoro, Momoyama-cho, Fushimi-ku, Kyoto 612 (JP).</b></p> <p>(74) Agents: <b>REED, T., David et al.; The Procter &amp; Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).</b></p>	<p>(81) Designated States: <b>AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</b></p> <p><b>Published</b>  <i>With international search report.</i></p>
<p>(54) Title: <b>MULTI-CATIONIC SILICONE POLYMERS</b></p> <p>(57) Abstract</p> <p>Disclosed are silicone polymers comprising: a) unit (A) and at least one of unit (B) and (C), wherein Q<sup>1</sup> is oxygen, nitrogen, sulfur or methylene; X is an integer of 0 to about 20; Y is an integer of 0 to about 20; Z is an integer of 0 to about 20; Q<sup>2</sup> is CH<sub>2</sub> or any of formulae: (a), (b), (c) or (d), R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are independently alkyl of 1 to 3 carbons, phenyl, benzyl, or phenethyl; R<sup>5</sup> is ethylene or propylene; R<sup>6</sup> is hydrogen, alkyl of 1 to 4 carbons, fluorocarbon of 1 to 4 carbons, phenyl, or benzyl; R<sup>7</sup> is alkyl of 1 to about 30 carbons, phenyl, benzyl, or phenethyl; Q<sup>3</sup> is OH, OR<sup>8</sup>, NH<sub>2</sub>, NHR<sup>9</sup>, SH, SR<sup>10</sup>, COOH, COOR<sup>11</sup>, or a halogen, wherein R<sup>8</sup>, R<sup>9</sup>, R<sup>10</sup>, and R<sup>11</sup> are alkyl or alkylene of 1 to about 20 carbons; n is an integer of 1 to about 500; and m is an integer of 1 to about 100; and b) a stoichiometric amount of an anion selected from the group consisting of anionic forms of sulfate, hydrosulfate, methylsulfate, carbonate, bicarbonate, chloride, bromide, iodide, and mixtures thereof. Further disclosed fabric treatment and hair care compositions comprising the multi-cationic silicone polymer. Still further disclosed are suitable methods of making the silicone polymers.</p>	
<div style="display: flex; justify-content: space-around; align-items: flex-start;"> <div style="text-align: center;"> <math display="block">\begin{array}{c} R^1 \\   \\ \text{---}[\text{SiO}]_n\text{---} \\   \\ R^2 \end{array} \quad (A)</math> </div> <div style="text-align: center;"> <math display="block">\begin{array}{c} R^3 \\   \\ \text{---Si---CH}_2\text{---}[(\text{CH}_2)_X\text{Q}^1(\text{CH}_2)_Y\text{Z}]_n\text{---Q}^2\text{---}(\text{N}^+\text{R}^5)_m\text{---Q}^3 \\   \\ R^4 \end{array} \quad (B)</math> </div> <div style="text-align: center;"> <math display="block">\begin{array}{c} R^3 \\   \\ \text{---Si---CH}_2\text{---}[(\text{CH}_2)_X\text{Q}^1(\text{CH}_2)_Y\text{Z}]_n\text{---Q}^2\text{---}(\text{N}^+\text{R}^5)_m\text{---Q}^3 \\   \\ \text{O} \end{array} \quad (C)</math> </div> <div style="display: flex; justify-content: space-around; width: 100%;"> <div style="text-align: center;"> <math display="block">\begin{array}{c} \text{---CH}_2\text{CH---} \\   \\ \text{CH}_2\text{OH} \end{array} \quad (a)</math> </div> <div style="text-align: center;"> <math display="block">\begin{array}{c} \text{---CH}_2\text{CHCH}_2\text{---} \\   \\ \text{OH} \end{array} \quad (b)</math> </div> <div style="text-align: center;"> <math display="block">\begin{array}{c} \text{---CH}_2\text{---} \text{C}_6\text{H}_4 \text{---} \text{C}(\text{OH})(\text{CH}_3)\text{---} \end{array} \quad (c)</math> </div> <div style="text-align: center;"> <math display="block">\begin{array}{c} \text{---CH}_2\text{---} \text{C}_6\text{H}_4 \text{---} \text{C}(\text{OH})(\text{CH}_3)\text{---} \end{array} \quad (d)</math> </div> </div> </div>	

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## MULTI-CATIONIC SILICONE POLYMERS

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### TECHNICAL FIELD

The present invention relates to a multi-cationic silicone polymer having  
10 water-miscible characteristics. The present invention further relates to fabric  
treatment and hair care compositions comprising the multi-cationic silicone  
polymer.

### BACKGROUND

15 Silicone polymers are used in various fields of industry due to their  
general characteristics such as ability to lower surface tension, lubricity, ability to  
suppress suds, ability to provide glossiness, thermal stability, chemical stability,  
and very low bioactivity to humans. Silicone polymers with various substituents  
of a wide range of molecular weight are used for fabric and hard-surface  
20 treatment products, cosmetic and toiletry products, and pharmaceutical products.  
Many of these products are based on solvents and carriers which have high  
polarity.

Silicone polymers which are designed to be miscible with water or suitable  
for cosmetic and fabric use are known in the art, such as in Kazama et al.  
25 "Syntheses and Reactions of Uniform Size Poly(Dimethylsiloxane) with Various  
Reactive End Groups" Polymer Journal Vol. 19, No. 9, pp1091-1100, issued  
March 26, 1987, U. S. Patent 4,659,777 issued April 21, 1987, Japanese Patent  
Laid-open (Kokai) H2-276824 published November 13, 1990, and Japanese  
Patent Laid-open (Kokai) H4-85334 and H4-85335 both published March 18,  
30 1992.

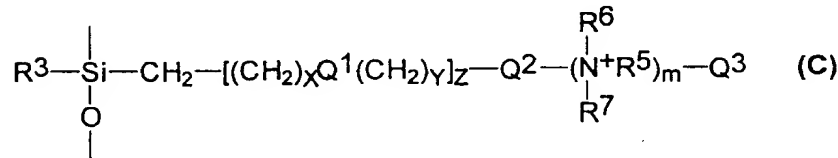
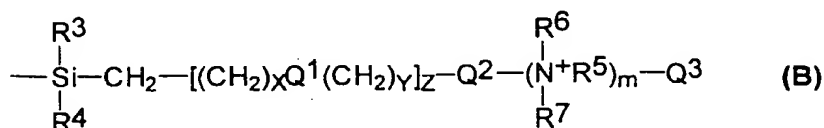
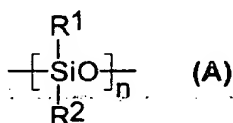
Generally, however, silicone polymers are difficult to dissolve or mix with  
solvents having high polarity, particularly water. Based on the foregoing, there is  
a need for a silicone polymer which is water miscible, and thus suitable for  
formulating in products based on solvents and carriers which have high polarity.

None of the existing-art provides all of the advantages and benefits of the present invention.

### SUMMARY

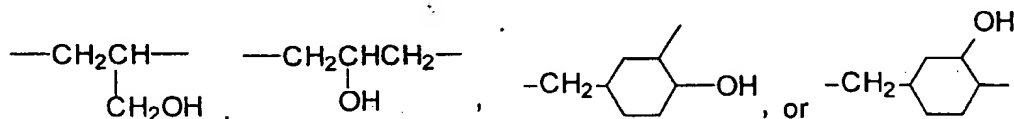
5 The present invention is directed to a multi-cationic silicone polymer comprising:

a) unit (A) and at least one of unit (B) and (C) of the following formulae:



10

wherein Q<sup>1</sup> is oxygen, nitrogen, sulfur or methylene; X is an integer of 0 to about 20; Y is an integer of 0 to about 20; Z is an integer of 0 to about 20; Q<sup>2</sup> is CH<sub>2</sub> or any of the following formulae:



15

R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> are independently alkyl of 1 to 3 carbons, phenyl, benzyl, or phenethyl; R<sup>5</sup> is ethylene or propylene; R<sup>6</sup> is hydrogen, alkyl of 1 to 4 carbons, fluorocarbon of 1 to 4 carbons, phenyl, or benzyl; R<sup>7</sup> is alkyl of 1 to about 30  
20 carbons, phenyl, benzyl, or phenethyl; Q<sup>3</sup> is OH, OR<sup>8</sup>, NH<sub>2</sub>, NHR<sup>9</sup>, SH, SR<sup>10</sup>,

COOH, COOR<sup>11</sup>, or a halogen, wherein R<sup>8</sup>, R<sup>9</sup>, R<sup>10</sup>, and R<sup>11</sup> are alkyl or alkylene of 1 to about 20 carbons; n is an integer of 1 to about 500; and m is an integer of 1 to about 100; and

- 5 b) a stoichiometric amount of an anion selected from the group consisting of anionic forms of sulfate, hydrosulfate, methylsulfate, carbonate, bicarbonate, chloride, bromide, iodide, and mixtures thereof.

The present invention is further directed to fabric treatment and hair care compositions comprising the multi-cationic silicone polymer.

10 The present invention is still further directed to a suitable method of making the multi-cationic silicone polymer.

These and other features, aspects, and advantages of the present invention will become evident to those skilled in the art from reading of the present disclosure.

15

#### DETAILED DESCRIPTION

While the specification concludes with claims particularly pointing and distinctly claiming the invention, it is believed the present invention will be better understood from the following description.

20 All percentages herein are by weight of the compositions unless otherwise indicated.

All ratios are weight ratios unless otherwise indicated.

25 All percentages, ratios, and levels of ingredients referred to herein are based on the actual amount of the ingredient by weight, and do not include solvents, fillers, or other materials with which the ingredient may be combined as commercially available products, unless otherwise indicated.

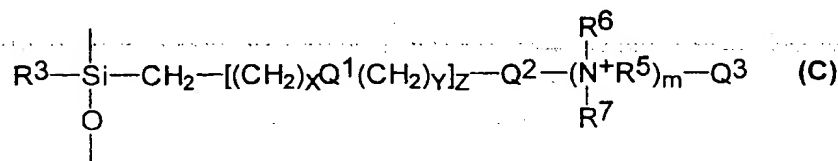
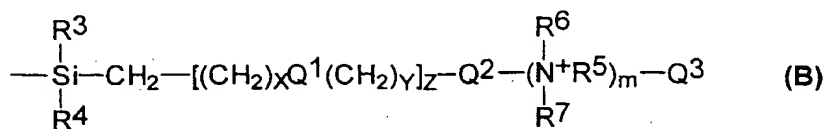
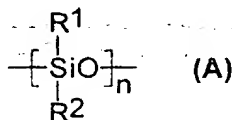
As used herein, "comprising" means that other steps and other ingredients which do not affect the end result can be added. This term encompasses the terms "consisting of" and "consisting essentially of".

30 All cited references are incorporated herein by reference in their entireties. Citation of any reference is not an admission regarding any determination as to its availability as prior art to the claimed invention.

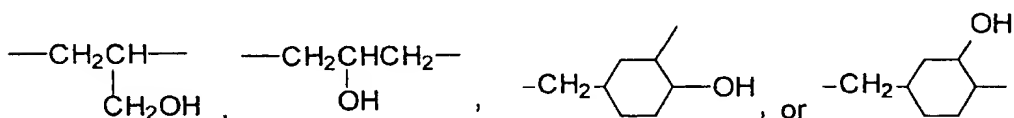
#### MULTI-CATIONIC SILICONE POLYMER

The multi-cationic silicone polymer of the present invention comprises:

- 35 a) unit (A) and at least one of unit (B) and (C) of the following formulae:



wherein Q<sup>1</sup> is oxygen, nitrogen, sulfur or methylene; X is an integer of 0 to about 20; Y is an integer of 0 to about 20; Z is an integer of 0 to about 20; Q<sup>2</sup> is CH<sub>2</sub> or any of the following formulae:



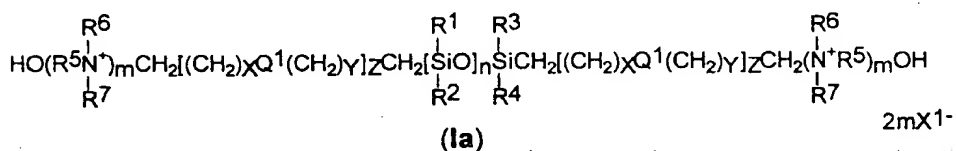
R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> are independently alkyl of 1 to 3 carbons, phenyl, benzyl, or phenethyl; R<sup>5</sup> is ethylene or propylene; R<sup>6</sup> is hydrogen, alkyl of 1 to 4 carbons, fluorocarbon of 1 to 4 carbons, phenyl, or benzyl; R<sup>7</sup> is alkyl of 1 to about 30 carbons, phenyl, benzyl, or phenethyl; Q<sup>3</sup> is OH, OR<sup>8</sup>, NH<sub>2</sub>, NHR<sup>9</sup>, SH, SR<sup>10</sup>, COOH, COOR<sup>11</sup>, or a halogen, wherein R<sup>8</sup>, R<sup>9</sup>, R<sup>10</sup>, and R<sup>11</sup> are alkyl or alkylene of 1 to about 20 carbons; n is an integer of 1 to about 500; and m is an integer of 1 to about 100; and

b) a stoichiometric amount of an anion selected from the group consisting of anionic forms of sulfate, hydrosulfate, methylsulfate, carbonate, bicarbonate, chloride, bromide, iodide, and mixtures thereof.

The multi-cationic silicone polymer of the present invention may comprise units (A) and (C) in a random order and (B) at a terminal, so long as at least one

unit of (A) and at least one of either unit (B) or unit (C) are present. The multi-cationic silicone polymers herein include at least one block cationic polyelectrolyte site as included in unit (B) or (C). With such a structure, the multi-cationic silicone polymer of the present invention can possess the characteristics of a silicone polymer as well as water-miscible characteristics of a cationic polymer. The structural design and molecular weight of the multi-cationic silicone polymer of the present invention may be selected by the artisan to obtain those according to the desired product to which the polymer is formulated. The multi-cationic silicone polymer of the present invention may terminate with an additional moiety or include adequate spacers as selected by the artisan to facilitate synthesis. The multi-cationic silicone polymer of the present invention can be terminated with unit (B), or with unit (A) or (C) end-capped with an alkyl or a trimethylsilicon. When unit (C) is included, the multi-cationic silicone polymer comprises a branched moiety, whereas when unit (C) is not included, the multi-cationic silicone polymer is linear.

The multi-cationic silicone polymer of the present invention may be made only from unit (A) and unit (B). When the multi-cationic silicone polymer of the present invention is made of one unit of (A) and 2 units of (B), the polymer includes 2 block cationic polyelectrolyte sites, and preferably takes the following general formula (Ia):

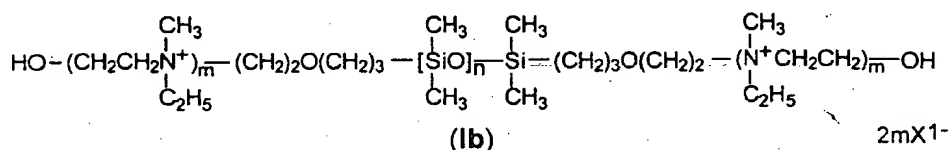


wherein Q<sup>1</sup> is oxygen, nitrogen, sulfur or methylene; X is an integer of 0 to about 20; Y is an integer of 0 to about 20; Z is an integer of 0 to about 20; R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> are independently alkyl of 1 to 3 carbons, phenyl, benzyl, or phenethyl; R<sup>5</sup> is ethylene or propylene; R<sup>6</sup> is hydrogen, alkyl, or fluorocarbon of 1 to 10 carbons, phenyl, or benzyl; R<sup>7</sup> is alkyl of 1 to about 30 carbons or phenyl, benzyl, or phenethyl; n is an integer of 1 to about 500; m is an integer of 1 to about 100; and X<sup>1</sup> is sulfate, hydrosulfate, methylsulfate, carbonate, bicarbonate, chloride, bromide, iodide, or mixtures thereof.

Preferably, Q<sup>1</sup> is oxygen or methylene; X is an integer of 0 to 5; Y is an integer of 0 to about 5; Z is an integer of 0 to about 10; R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> are

the same substituents wherein the substituent is an alkyl of 1 to 3 carbons or a phenyl, more preferably methyl; R<sup>5</sup> is ethylene or propylene; R<sup>6</sup> is hydrogen, methyl, ethyl, phenyl, or benzyl, more preferably methyl or ethyl; R<sup>7</sup> is alkyl of 1 to about 30 carbons, preferably methyl or ethyl; n is an integer of 5 to about 500  
 5 more preferably 5 to about 200; and m is an integer of 3 to about 100; and X<sup>1</sup> is sulfate, hydrosulfate, methylsulfate, carbonate, bicarbonate, chloride, bromide, iodide, or mixtures thereof.

Still preferred are silicone polymers of the following general formula (Ib):



wherein n is an integer of from about 5 to about 100, m is an integer of 3 to about 20, and X<sup>1</sup> is selected from the group consisting of sulfate, hydrosulfate, methylsulfate, carbonate, hydrocarbonate, chloride, bromide, iodide, and  
 15 mixtures thereof.

#### RING-OPENING POLYMERIZATION

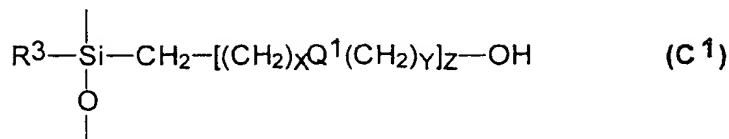
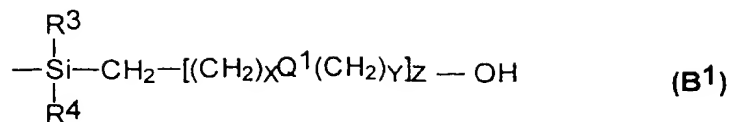
The multi-cationic silicone polymers of the present invention can be prepared by a synthesis route comprising three stages.

The first stage comprises ring-opening polymerization of an activated  
 20 siloxane.

The first stage may further comprise a preliminary stage of preparing an activated siloxane. The activated siloxane is a siloxane compound having its terminals substituted with a sulfonic ester or a halogen, preferably tosyl or mesyl sulfonic ester groups.

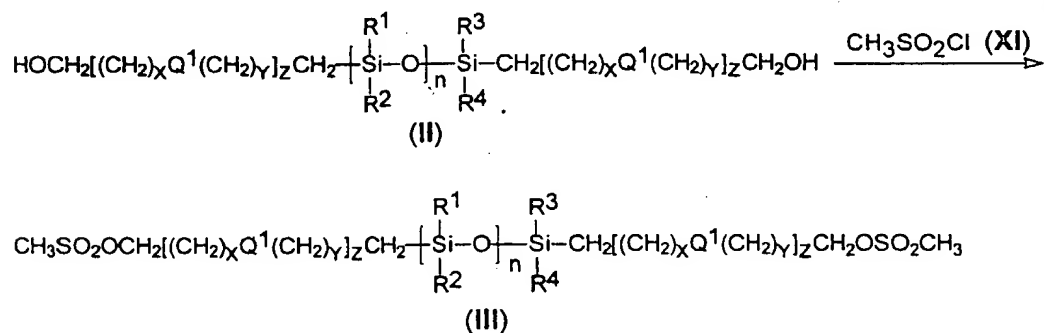
25 The starting silicone material to make this activated siloxane can be any linear or branched silicone having hydroxy functionality, wherein any other existing functionality are non-reactive with the below mentioned activating agents, nor the below mentioned cyclic iminoethers. The starting silicone material are those comprising unit (A) mentioned above and at least one of units  
 30 (B<sup>1</sup>) and (C<sup>1</sup>) of the following formulae:





- wherein Q<sup>1</sup> is oxygen, nitrogen, sulfur or methylene; X is an integer of 0 to about 20; Y is an integer of 0 to about 20; Z is an integer of 0 to about 20; and R<sup>3</sup> and R<sup>4</sup> are independently alkyl of 1 to 3 carbons, phenyl, benzyl, or phenethyl. The starting silicone material can be any known in the art so long as at least one of the terminals is hydroxy. Preferably, the starting silicone material is a hydroxyalkyl-siloxane, hydroxyalkoxyalkyl-siloxane, and polyalkoxyl-siloxane.
- Examples of commercially available starting silicone materials are; X-22-160AS, KF-6001, KF-6002, KF-6003, X-22-4015, X-22-4901, KF-353, KF-354, KF-355, KF-945, and KF-6011 supplied by Shin-Etsu Chemical, SF8427, BY16-005, BY16-007, SH3746, SF8428, SH3771, BY16-036, BY16-027, and BY16-848 supplied by Toray Dow Corning Silicone, TSF4750, TSF4751, XF42-B0970, SF1188, SF1288, and SF1388 supplied by Toshiba Silicone.

An embodiment of preparation of an activated siloxane is shown in the following scheme:

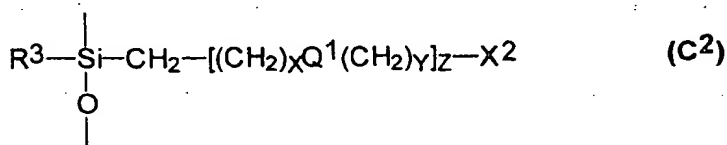
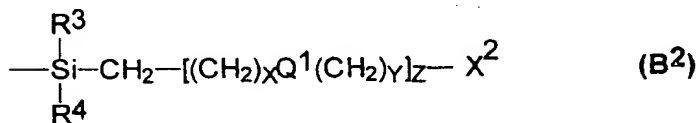


The starting silicone material as exemplified by dihydroxy-terminated polyalkylsiloxane as shown by formula (II) is subjected to the reaction with an

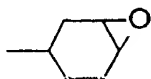
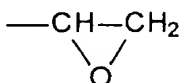
activating agent to obtain an activated siloxane as shown by formula (III). The activating agent is selected from the group consisting of sulfonic halide, wherein halide is a chloride, bromide, or iodide,  $P(Hal)_3$ ,  $P(Hal)_5$  and  $SO_2(Hal)_2$  or mixtures thereof; wherein (Hal) is a halogen selected from chloride, bromide, or iodide. Preferable activating agents are tosyl chloride and mesyl chloride. Mesyl chloride is exemplified as formula (XI).

Suitable mediums for carrying out this first stage of synthesis include inert solvents which provide an anhydrous condition. Exemplary inert solvents are absolute (hereinafter referred to as "abs.") tetrahydrofuran (hereinafter referred to as "THF"), abs. benzene, abs. toluene, abs. triethylamine, abs. pyridine, and mixtures thereof. Preferably, the medium contains a Lewis base. Exemplary Lewis bases include those which are liquid and solid such as abs. triethylamine, abs. pyridine, dimethylamino pyridine (hereinafter referred to as "DMAP"), and 1,8-diazabicyclo[5.4.0.]-7-undecene (hereinafter referred to as "DBU"). Abs. triethylamine and abs. pyridine act both as a solvent and a liquid Lewis base, and thus suitable. Abs. triethylamine is a highly suitable liquid Lewis base. More preferably, the medium contains at least a stoichiometric amount to the activating agent of a Lewis base, as it provides good yield. Still preferably, the medium contains: a volatile solvent such as abs. THF, abs. benzene, abs. toluene and mixtures thereof; and a stoichiometric amount to the activating agent of a liquid Lewis base such as abs. triethylamine, abs. pyridine, and mixtures thereof. The reaction can be carried out at room temperature at atmospheric pressure.

Alternatively, the activated siloxane can be any linear or branched silicone having halogen or epoxy functionalities, wherein any other existing functionalities are non-reactive with the below mentioned cyclic iminoethers. The activated siloxane are those comprising unit (A) mentioned above and at least one of unit (B<sup>2</sup>) or (C<sup>2</sup>) of the following formulae:

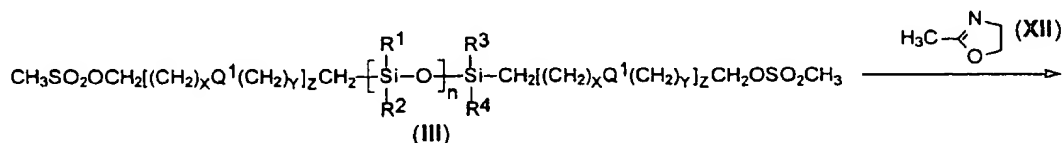


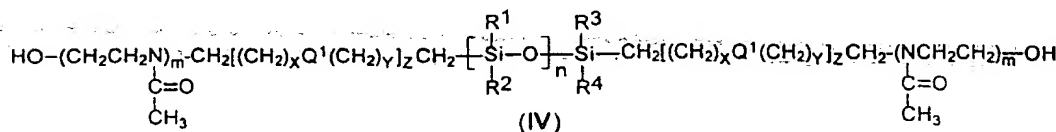
wherein Q<sup>1</sup> is oxygen, nitrogen, sulfur or methylene; X is an integer of 0 to about 20; Y is an integer of 0 to about 20; Z is an integer of 0 to about 20; R<sup>3</sup> and R<sup>4</sup> are independently alkyl of 1 to 3 carbons, phenyl, benzyl, or phenethyl; and X<sup>2</sup> is a halide or an epoxy of the following formulae:



The activated siloxane can be any known in the art so long as it has at least one halogen or epoxy functionality. The epoxy functionality can be a glycidyl-type or oxirane-type. Preferably, the activated siloxane has halogen functionalities. When these halogen terminated activated siloxane are used directly for ring-opening polymerization, the above mentioned reaction with the activating agents are unnecessary. Examples of commercially available siloxane compounds with halogen functionalities which may be used directly as activated siloxane are; LMS-152 supplied by AZmax Co., Ltd., TSL9236, TSL9276, TSL9226, and TSL9206 supplied by Toshiba Silicone. Commercially available siloxane compounds having epoxy functionalities are; KF-105, X-22-163A, X-22-163B, X-22-163C, KF-1001, KF-101, X-22-169AS, X-22-169B, KF-102, and X-22-173DX supplied by Shin-Etsu Chemical, SF8411, SF8413, BY16-855, BY16-855B, BY16-839, SF8421EG, and BY16-845 supplied by Toray Dow Corning Silicone, YF3965, XF42-A4439, TSF4730, XF42-A4438, XC96-A4462, XC96-A4463, XC96-A4464, XF42-A5041, TSL9946, TSL9986, and TSL9906 supplied by Toshiba Silicone.

The activated siloxane either obtained by the preliminary reaction or obtained commercially is polymerized through a reaction known as ring-opening polymerization, an embodiment of which is shown in the following scheme:





This can be done by subjecting the activated siloxane as exemplified by formula (III) with a cyclic iminoether to obtain a polyamide siloxane exemplified by formula (IV). The cyclic iminoether is selected from the group consisting of 2-substituted-2-oxazoline, 2-substituted-5,6-dihydro-4H-1,3-oxazine, and mixtures thereof. Preferable cyclic iminoethers are 2-Z'-2-oxazoline and 2-Z'-oxazine wherein Z' is a hydrogen, alkyl, or fluorocarbon having 1 to 10 carbons, phenyl and benzyl, still preferable are 2-alkyl-2-oxazoline wherein the alkyl is made of 1 to 3 carbons, as exemplified as formula (XII). The tosyl, mesyl or halide group of the activated siloxane (III) is known to be a leaving group on the attack by various nucleophilic monomers. The tosyl and mesyl groups are preferable leaving groups. Thus, the activated siloxane (III) is utilized as a macromolecular initiator for the synthesis of a block copolymer through nucleophilic reaction toward the tosylate or mesylate ester function or halide at the functionality by the cyclic iminoether which acts as a nucleophilic monomer. The polyamide siloxane (IV) thus obtained has concentrated polyamide moieties at functionalities of the polymer which had originally been activated.

Suitable mediums for carrying out this first stage of synthesis include inert solvents which provide an anhydrous condition. Exemplary inert solvents are abs. acetonitrile, abs. THF, abs. benzene, abs. toluene, abs. triethylamine, abs. pyridine, and mixtures thereof. Preferably, the medium contains a Lewis base. Exemplary Lewis bases include those which are liquid and solid such as abs. triethylamine, abs. pyridine, dimethylamino pyridine (hereinafter referred to as "DMAP"), and 1,8-diazabicyclo[5.4.0]-7-undecene (hereinafter referred to as "DBU"). Abs. triethylamine and abs. pyridine act both as a solvent and a liquid Lewis base, and thus suitable. Abs. triethylamine is a highly suitable liquid Lewis base. More preferably, the medium contains at least a stoichiometric amount to the activated siloxane (III) of a Lewis base. It has been found that the existence of this amount of Lewis base significantly raises the conversion yield of the activated siloxane (III) to the resulting polyamide siloxane. Thus, the number of amide moieties of the present polymers (number "m" in the structure) can be controlled with significantly improved precision to provide the targeted polymer at

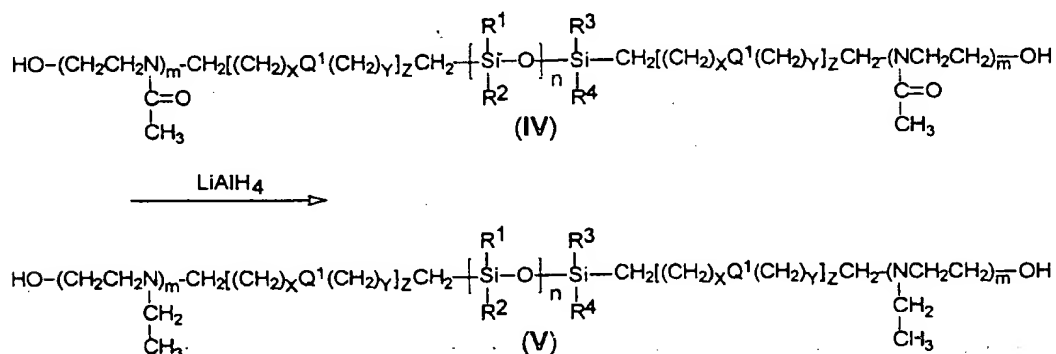
high yield. Still preferably, the medium contains: a volatile solvent such as abs. acetonitrile, abs. THF, abs. benzene, abs. toluene and mixtures thereof; and a stoichiometric amount to the activating agent of a liquid Lewis base such as abs. triethylamine, abs. pyridine, and mixtures thereof. A highly preferred medium is an acetonitrile solution of at least a stoichiometric amount to the activated siloxane of abs. triethylamine. The reaction can be carried out at room temperature or elevated temperature at around atmospheric pressure.

After the ring-opening polymerization is completed, the obtained reactant is treated with an alkali or alkali salt to obtain the polyamide siloxane (IV). Such alkali or alkali salt include sodium carbonate, sodium hydrogen carbonate, potassium carbonate, potassium hydrogen carbonate, amines in an inert solvent, and metal or tetra-alkyl ammonium salts of organic acids. When the reactant is treated with aqueous alkaline such as sodium carbonate, the finally obtained polymer will have a hydroxy terminal. When the reactant is treated with amines in an inert solve, the finally obtained polymer will have amine or ammonium terminated terminals. When the reactant is treated with salts of organic acids, the finally obtained polymer will have carboxylate or ester terminals.

#### REDUCTION OR HYDROLYSIS

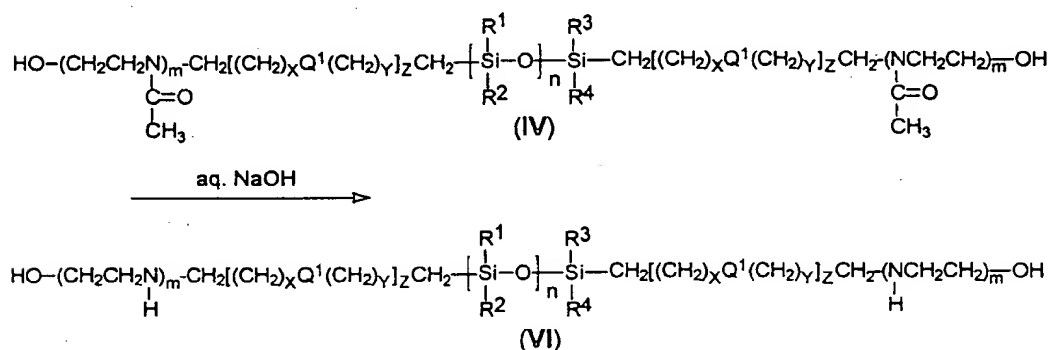
The second stage comprises reduction or hydrolysis of the obtained polyamide siloxane (IV).

Reduction can be done, for example, by reacting the polyamide siloxane with a reducing agent such as  $\text{LiAl}(\text{OR})_x\text{H}_{4-x}$  wherein R is methyl, ethyl, or isopropyl, and x is 0 or an integer from 1 to 3; preferably  $\text{LiAlH}_4$  (lithium aluminum hydride) to obtain a reduced polyamide siloxane as exemplified by formula (V) as shown in the following scheme:



Suitable mediums for carrying out such reduction include inert solvents such as abs. THF and abs. diethylether. Reduction can be alternatively done by reacting the polyamide siloxane with an agent such as  $(C_2H_5)_3O^+BF_4^-$ ,  $Cl_3SiH$ ,  $Cl_3SiOH$ ,  $Cl_3SiOCH_3$ ,  $Cl_3SiOC_2H_5$ ,  $(CH_3)_3SiCl$ , or dimethylsulfate in an inert solvent such as n-hexane or  $CH_2Cl_2$ , followed by treatment with  $NaBCNH_3$  or  $NaBH_4$  in diethylether, ethanol, or THF.

Hydrolysis can be done, for example, by reacting the polyamide siloxane with aqueous and alcohol/aqueous solutions of strong acids and alkalis such as HCl, NaOH, KOH, or  $NaHCO_3$  to obtain a hydrolyzed polyamide siloxane as exemplified by formula (VI) as shown in the following scheme:



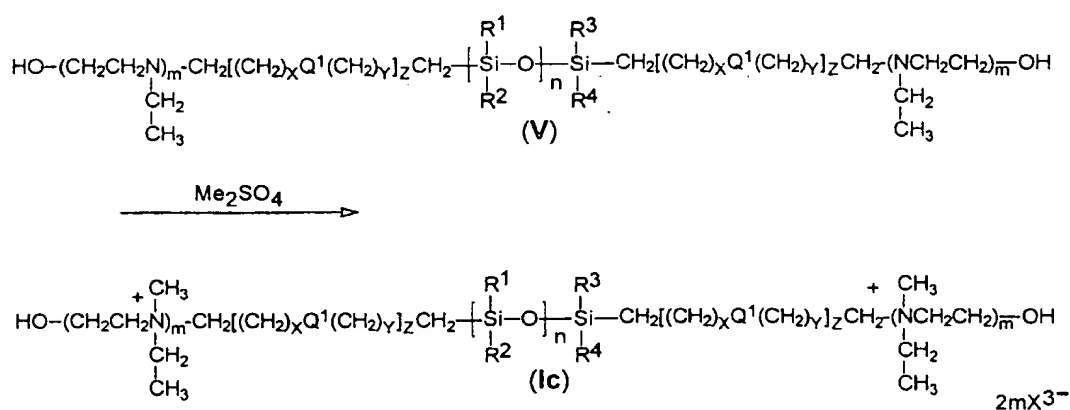
Hydrolysis can be alternatively done by reacting the polyamide siloxane with an agent such as  $(C_2H_5)_3O^+BF_4^-$ ,  $Cl_3SiH$ ,  $Cl_3SiOH$ ,  $Cl_3SiOCH_3$ ,  $Cl_3SiOC_2H_5$ ,  $(CH_3)_3SiCl$ ,  $H_2N-NH_2$ , or dimethylsulfate in an inert solvent such as abs. THF, diethylether, n-hexane or  $CH_2Cl_2$ , followed by treatment with diluted aqueous solutions of acids or alkalis such as HCl, NaOH, KOH,  $NaHCO_3$ ,  $K_2CO_3$ ,  $Na_2CO_3$ , or  $KHCO_3$ .

#### QUATERNIZATION

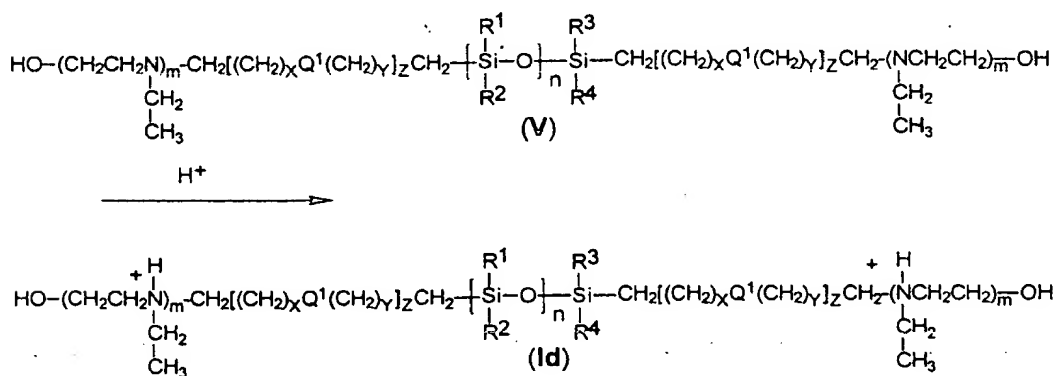
The third stage comprises quaternization of the obtained reduced polyamide siloxane (V) or hydrolyzed polyamide siloxane (VI) to obtain a multi-cationic siloxane polymer of the present invention.

This can be carried out by adding a quaternizing agent. Quaternizing agents are selected from the group consisting of monomethylsulfuric acid, dimethylsulfate, diethylsulfate, dimethylcarbonate, methylchloride, methyliodide, methylbromide, ethylchloride, ethyliodide, ethylbromide, benzylchloride,

benzylbromide, benzyl iodide, sulfuric acid, carboxylic acid, hydrochloric acid, hydrobromic acid, hydroiodic acid, and mixtures thereof. It is known in the art that, when quaternization is conducted with quaternizing agents which provide positively charged alkyls such as monomethylsulfuric acid, dimethylsulfate, diethylsulfate, dimethylcarbonate, methylchloride, methyl iodide, methylbromide, ethylchloride, ethyl iodide, ethylbromide, benzylchloride, benzylbromide, and benzyl iodide, the quaternized cite is stable and pH independent. Quaternization which provides positively charged alkyls is exemplified by the following scheme:



On the other hand, when quaternization is conducted with quaternizing agents which provide protons to the amine moiety such as sulfuric acid, carboxylic acid, hydrochloric acid, hydrobromic acid, and hydroiodic acid, the quaternized cite is pH dependent. Quaternization which provides protons to the amine is exemplified by the following scheme:



The quaternizing agent may be selected according to the desired characteristic of the final multi-cationic silicone polymer.

#### USE OF MULTI-CATIONIC SILICONE POLYMER

5 The multi-cationic silicone polymers of the present invention are believed to possess physical properties of both a silicone polymer and a cationic polymer. Specifically, the multi-cationic sites are believed to provide the multi-cationic silicone polymers herein to be water miscible, provide good deposition and/or adhesion to various substrates, and provide antibacterial effects. It is also  
10 believed that the multi-cationic silicone polymers herein provide useful characteristics of a silicone polymer.

The multi-cationic silicone polymers herein are useful in various field and employed in various products. Non-limiting examples of its useful fields include: consumer products area, medical and pharmaceutical area, fabrics area, and other industrial and chemical areas.

15 In the area of consumer products, the multi-cationic silicone polymers herein are suitable for: treating, conditioning, polishing or providing antibacterial activity to; laundry products, hair care products, skin care products, and hard surface treating products. More specifically, the multi-cationic silicone polymers herein are suitable for: conditioning, softening, anti-wrinkle, anti-static, anti-  
20 bacterial, and soil anti-redeposition of laundry products such as laundry detergents, soaps, fabric cleaners, fabric conditioners, fabric static controlling products, and fabric wrinkle controlling products; conditioning, anti-static, anti-bacterial, and fixative agents for hair care products such as shampoos, hair conditioners, hair treatments, hair sprays, and hair mousses; lubricating and  
25 deodorizing for skin care products such as cosmetics and antiperspirants; polishing, lubricating, and anti-bacterial for hard surface treating products such as furniture treating products, kitchen cleaners, and automobile cleaners or polishers; and for viscosity building or for providing controlled-release of active material or perfumes for any of the above.

30 In the medical and pharmaceutical area, the multi-cationic silicone polymers herein are useful for adhesive for transdermal delivery of actives, immobilized preparations, dental impressions, and anti-carries agents in dental/oral care formulations.

35 In other industrial and chemical areas, the multi-cationic silicone polymers herein are useful for algicides, anti-mold, anti-microbial, deodorizing, coating,



mold-release, anti-friction, anti-foaming, anti-static, and for blending for composites.

The multi-cationic silicone polymers of the present invention are particularly useful for products which are based on solvents and carriers of high polarity, particularly water, and which are aimed to deposit on a substrate. Because of their water miscible nature, and multi-cationic sites, the multi-cationic silicone polymers of the present invention are thought to provide good deposition to the surface of substrates such as fabric, hair, skin, and hard-surfaces, particularly fabric and hair. Further, these multi-cationic silicone polymers provide bactericide effects to the aqueous formulations to which it is added.

The present invention further relates to fabric treatment compositions comprising the multi-cationic silicone polymer. The multi-cationic silicone polymer of the present invention is useful for fabric treatment compositions, particularly those which comprise water as a carrier. These fabric treatment compositions preferably comprise about 0.01% to about 30% of the multi-cationic silicone polymer, and a suitable carrier. Suitable carriers include water, ethanol, isopropanol, 1,2-propanediol, 1,3-propanediol, propylene carbonate, and mixtures thereof. In addition, other components such as quaternary ammonium softening agents, brighteners, dispersibility aids, amine oxides, stabilizers, soil releasing agents, scum dispersants, and chelating agents can be comprised. The fabric treatment compositions of the present invention provide anti-wrinkle benefit, softness, and antistatic benefit to the fabric which is treated.

The present invention further relates to hair care compositions comprising the multi-cationic silicone polymer. The multi-cationic silicone polymer of the present invention is useful for hair care compositions, particularly those which comprise water as a carrier. The hair care compositions preferably comprise about 0.01% to about 30% of the multi-cationic silicone polymer, and a suitable carrier. Suitable carriers include water, lower alkyl alcohols, polyhydric alcohols, and mixtures thereof. The lower alkyl alcohols useful herein are C<sub>1</sub>-C<sub>6</sub> alkyl monohydric alcohols, preferably C<sub>2</sub>-C<sub>3</sub> alkyl alcohols. The preferred lower alkyl alcohol is ethyl alcohol, isopropyl alcohol, and mixtures thereof. The polyhydric alcohols useful herein include, for example, propylene glycol, hexylene glycol, glycerin, and propane diol, and mixtures thereof. The hair care composition of the present invention may further comprise an additional hair care active such as deterative surfactants, conditioning agents, and fixative polymers. The multi-

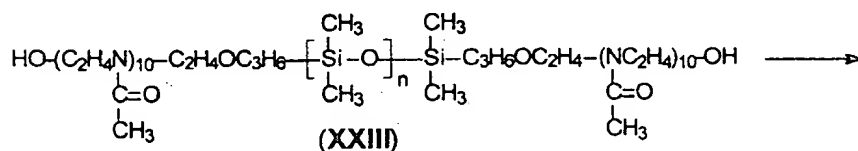
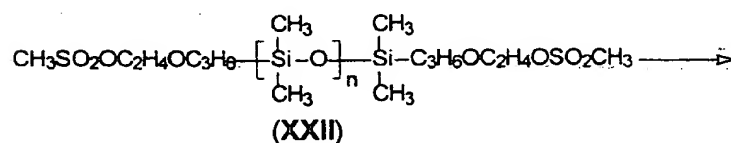
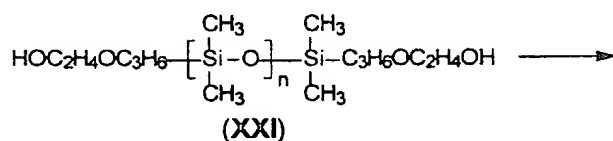
cationic silicone polymer is particularly useful for making hair conditioning compositions further containing an additional conditioning agent selected from the group consisting of solid and liquid fatty compounds such as fatty alcohols, fatty acids, fatty acid derivatives, fatty alcohol derivatives, and steroids, solid and liquid hydrocarbons, cationic surfactants, other cationic polymers, and other silicone compounds. The hair care compositions of the present invention provide conditioning benefit and antistatic benefit to the hair which is treated.

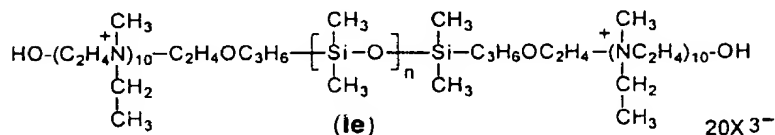
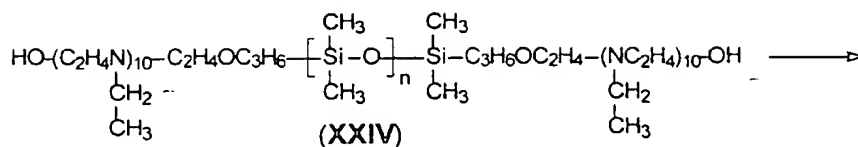
### EXAMPLES

The following examples further describe and demonstrate the preferred embodiments within the scope of the present invention. The examples are given solely for the purpose of illustration and are not to be construed as limitations of the present invention since many variations thereof are possible without departing from the spirit and scope of the invention. Ingredients are identified by chemical name, or otherwise defined below.

#### EXAMPLE 1

The polymer with formula (Ie) is suitably obtained by a synthesis route as shown in the following scheme:





- 5  $\text{X}^{3-}$  = mixture of anions selected from the group consisting of  $\text{SO}_4^{2-}$ ,  $\text{HSO}_4^-$ , and  $\text{CH}_3\text{SO}_4^-$

#### Activation

10 A 60 mmole portion of mesyl chloride (1.5 equivalent) is added dropwise to an ice-cooled stirring solution of 20 mmole dihydroxy polysiloxane having an average 90 to 110 units (XXI) and 60 mmole triethylamine (1.5 equivalent) in 120 ml of abs. THF. The reaction mixture is stirred for 1 hour under ice-cooling and for 1 day at room temperature. Removal of THF in vacuo after filtration is followed by the addition of 100 ml of ice water to the residue. This mixture is extracted with chloroform and the chloroform extract is washed with aq. sat.  $\text{NaHCO}_3$  and dried with anhydrous sodium sulfate. This syrup is further treated according to common treatment to obtain a mesyl derivative of polysiloxane (XXII).

#### Ring-opening polymerization

20 A sealed reaction mixture of a 5.440 g portion of the obtained mesyl siloxane (XXII) (5 mmole), 100 mmole distilled 2-methyl-2-oxazoline and 10 mmole triethylamine in 50 ml of anhydrous acetonitrile in a sealed tube is stirred at  $80^\circ\text{C}$  for 24 hours. The reaction mixture is then cooled to room temperature and 20 ml of 10% sodium carbonate is added with stirring. The mixture is stirred for 2 hours, then the mixture is concentrated in vacuo. The mixture is extracted with chloroform and the chloroform extract is dried with anhydrous sodium sulfate. This syrup is further treated according to common treatment to obtain a polyamide siloxane (XXIII).

Reduction

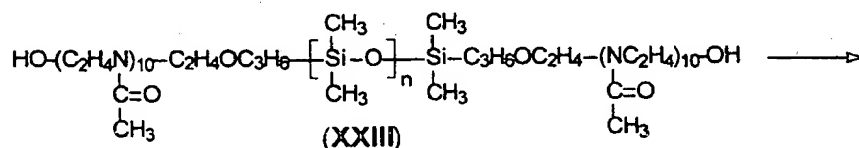
An abs. benzene (50 ml) solution of the obtained polyamide siloxane (XXIII) (0.91 mmole) is added dropwise to an ice-cooled stirring mixture of 29 mmole (3.2 equivalent) lithium aluminum hydride and 50 ml of abs. THF. After the addition is complete the reaction mixture is stirred in ice bath for an additional hour, then the temperature is increased gradually until the reaction mixture reaches reflux, then continued stirring under reflux for 1 day. The reaction mixture is then cooled to room temperature and 10 ml of water is added with stirring. The mixture is stirred for an hour, then the mixture is filtered. The residue is washed with hot chloroform and is extracted with chloroform under reflux 3 times. The combined filtrate are dried with anhydrous sodium sulfate. This syrup is further treated according to common treatment to obtain a N-alkyl polyethyleneimino siloxane (XXIV).

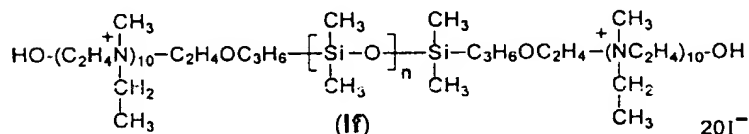
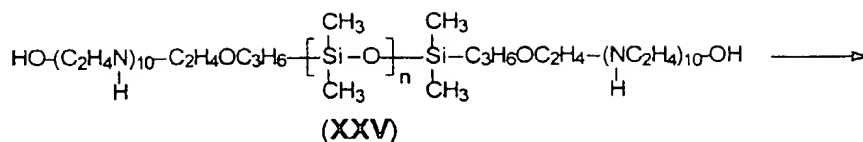
Quaternization

A 8.1 g portion of the obtained N-alkyl polyethyleneimino siloxane (XXIV) is dissolved in 50 ml hexane and is treated with 3.2 g sodium hydrogen carbonate and 20 ml of water in ice bath cooling. To this mixture is added 4.4 g of dimethyl sulfate dropwise over a period of twenty minutes at 0°C. After the addition is complete the reaction mixture is stirred in ice bath for an additional hour, then the temperature is increased gradually until the reaction mixture reaches reflux, then continued stirring under reflux overnight. The reaction mixture is then cooled to room temperature and the hexane layer is separated and washed with sat. aq. NaHCO<sub>3</sub> and water 3 times. The aqueous layer is extracted with chloroform. The combined hexane extracts and chloroform extracts are dried with anhydrous sodium sulfate. This syrup is further treated according to common treatment to obtain a multi-cationic silicone polymer (Ie).

EXAMPLE 2

The polymer with formula (If) is suitably obtained using the polyamide siloxane XXIII as shown in Example 1 by a synthesis route as shown in the following scheme:





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Hydrolysis

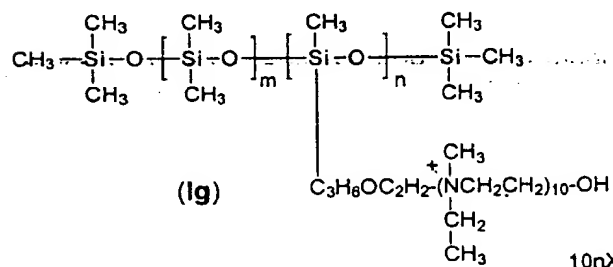
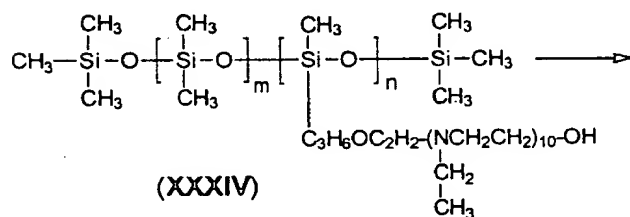
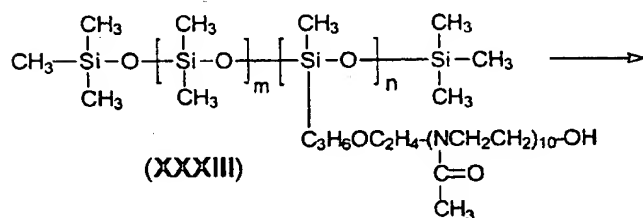
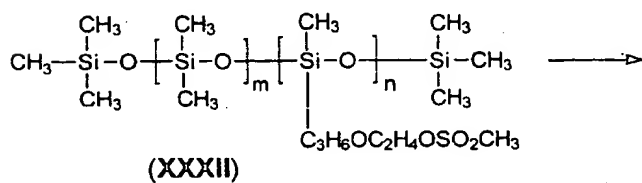
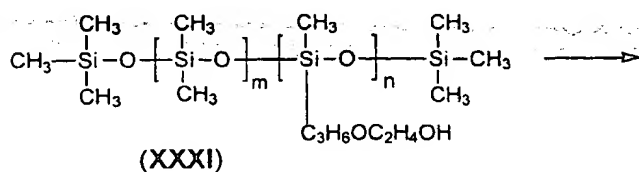
A 20 mL portion of triethyloxonium tetrafluoroborate (1M in dichloromethane) is added dropwise over a thirty minute period to a dichloromethane solution (100 mL) of 2.0 g of polyamide siloxane (XXIII) (0.8 mmole, 1.6 mmole equivalent). The reaction mixture was allowed to stir at room temperature for 24 hours. The dichloromethane slurry of polyiminiumsiloxane salt is poured slowly over a 150 mL ice-cold solution of 10% Na<sub>2</sub>CO<sub>3</sub>. Any solids remaining in the flask are treated with a 30 mL of 10% Na<sub>2</sub>CO<sub>3</sub> and combined with the original mixture. The entire mixture is extracted with dichloromethane and dried with Na<sub>2</sub>SO<sub>4</sub>. This syrup is further treated according to common treatment to give a two-phased oil which is identified spectroscopically as formula (XXV).

Quaternization

A 1.5 g portion of (XXV) was dissolved in 50 mL abs. ethanol and was treated with a 2 g of potassium hydrogen carbonate. To this mixture is added a mixture of 7 g methyl iodide in 10 mL abs. ethanol dropwise over a period of twenty minutes. The reaction mixture was allowed to stir at room temperature for 24 hours. Solvent of this solution was removed in vacuo to give a solid material whose spectroscopic data identified the material as multi-cationic silicone polymer of formula (If).

EXAMPLE 3

The polymer with formula (Ig) is suitably obtained by a synthesis route as shown in the following scheme:

10nX<sup>3-</sup>

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X<sup>3-</sup> = mixture of anions selected from the group consisting of SO<sub>4</sub><sup>2-</sup>, HSO<sub>4</sub><sup>-</sup>, and CH<sub>3</sub>SO<sub>4</sub><sup>-</sup>

### Activation

A 90 mmole portion of mesyl chloride (1.5 equivalent) is added dropwise to an ice-cooled stirring solution of 20 mmole branched carbinol polysiloxane having an average 50 to 70 units (structure XXXI) and 90 mmole triethylamine (1.5 equivalent) in 120 ml of abs. THF. The reaction mixture is stirred for 1 hour under ice-cooling and for 1 day at room temperature. Removal of THF in vacuo after filtration is followed by the addition of the 100 ml of ice water to the residue. This mixture is extracted with chloroform 3 times and the combined chloroform extracts are washed with aq. sat.  $\text{NaHCO}_3$  sol. and dried with anhydrous sodium sulfate. This syrup is further treated according to common treatment to obtain a mesyl derivative of polysiloxane (XXXII).

### Ring-opening polymerization

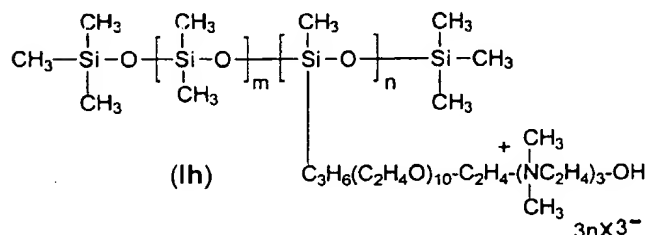
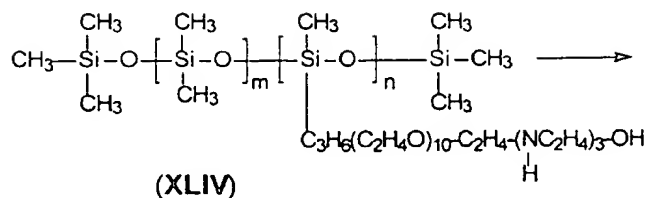
A sealed reaction mixture of a 5 mmole portion of the obtained mesyl siloxane (XXXII), 150 mmole distilled 2-methyl-2-oxazoline and 15 mmole triethylamine in 50 ml of anhydrous acetonitrile in a sealed tube is stirred at 80°C for 24 hours. The reaction mixture is then cooled to room temperature and 20 ml of 10% sodium carbonate is added with stirring. The mixture is stirred for 2 hours, then the mixture is concentrated in vacuo. The mixture is extracted with chloroform and the chloroform extract is dried with anhydrous sodium sulfate. This syrup is further treated according to common treatment to obtain a polyamide siloxane (XXXIII).

### Reduction

An abs. benzene (50 ml) solution of the obtained polyamide siloxane (XXXIII) (0.91 mmole) is added dropwise to an ice-cooled stirring mixture of 29 mmole (3.2 equivalent) lithium aluminum hydride and 50 ml of abs. THF. After the addition is completed the reaction mixture is stirred in ice bath for an additional hour, then the temperature is increased gradually until the reaction mixture reaches reflux, then continued stirring under reflux for 1 day. The reaction mixture is then cooled to room temperature and 10 ml of water is added with stirring. The mixture is stirred for a hour, then the mixture is filtered. The residue is washed with hot chloroform and is extracted with chloroform under reflux 3 times. The combined filtrates are dried with anhydrous sodium sulfate. This syrup is further treated according to common treatment to obtain a N-alkyl polyethyleneimino siloxane (XXXIV).







$\text{X}^{3-}$  = mixture of anions selected from the group consisting of  $\text{SO}_4^{2-}$ ,  $\text{HSO}_4^-$ , and  $\text{CH}_3\text{SO}_4^-$

The multi-cationic silicone polymer embodiments disclosed and represented by the previous examples have many advantages. For example, they provide good deposition to the surface of fabric and hair, and provide bactericide effects when included in aqueous compositions. When incorporated in fabric treatment compositions, they provide anti-wrinkle benefit, softness, and anti-static benefit. When incorporated in hair conditioner compositions, they provide conditioning benefit and anti-static benefit.

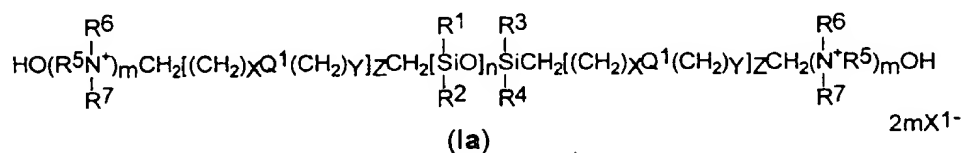
It is understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to one skilled in the art without departing from its spirit and scope.



b) a stoichiometric amount of an anion selected from the group consisting of anionic forms of sulfate, hydrosulfate, methylsulfate, carbonate, bicarbonate, chloride, bromide, iodide, and mixtures thereof.

2. The silicone polymer according to Claim 1 consisting of one or more of unit (A) and one or more of unit (B).

3. The silicone polymer according to Claim 2 having the following general formula (Ia):



5

wherein Q<sup>1</sup> is oxygen, nitrogen, sulfur or methylene; X is an integer of 0 to about 20; Y is an integer of 0 to about 20; Z is an integer of 0 to about 20; R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> are independently alkyl of 1 to 3 carbons, phenyl, benzyl, or phenethyl; R<sup>5</sup> is ethylene or propylene; R<sup>6</sup> is hydrogen, alkyl, or fluorocarbon of 1 to 10 carbons, phenyl, or benzyl; R<sup>7</sup> is alkyl of 1 to about 30 carbons or phenyl, benzyl, or phenethyl; n is an integer of 1 to about 500; m is an integer of 1 to about 100; and X<sup>1</sup> is sulfate, hydrosulfate, methylsulfate, carbonate, bicarbonate, chloride, bromide, iodide, or mixtures thereof.

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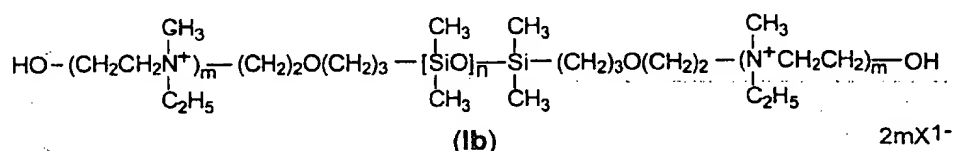
4. The silicone polymer according to Claim 3 wherein Q<sup>1</sup> is oxygen or methylene; X is an integer of 0 to 5; Y is an integer of 0 to about 5; Z is an integer of 0 to about 10; R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> are the same substituents wherein the substituent is an alkyl of 1 to 3 carbons or a phenyl; R<sup>5</sup> is ethylene or propylene; R<sup>6</sup> is hydrogen, methyl, ethyl, phenyl, or benzyl, R<sup>7</sup> is alkyl of 1 to about 30 carbons; n is an integer of 5 to about 500; m is an integer of 3 to about 100; and X<sup>1</sup> is sulfate, hydrosulfate, methylsulfate, carbonate, bicarbonate, chloride, bromide, iodide, or mixtures thereof.

5

5. The silicone polymer according to Claim 4 wherein Q<sup>1</sup> is oxygen or methylene; X is an integer of 0 to 5; Y is an integer of 0 to about 5; Z is an integer of 0 to about 10; R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> are all methyl; R<sup>5</sup> is ethylene or

propylene;  $R^6$  is methyl or ethyl;  $R^7$  is methyl or ethyl;  $n$  is an integer of 5 to about 200;  $m$  is an integer of 3 to about 100; and  $X^1$  is sulfate, hydrosulfate, methylsulfate, carbonate, bicarbonate, chloride, bromide, iodide, or mixtures thereof.

6. The silicone polymer according to Claim 5 having the following formula (1b):



wherein  $n$  is an integer of from about 5 to about 100,  $m$  is an integer of 3 to about 20, and  $X^1$  is selected from the group consisting of sulfate, hydrosulfate, methylsulfate, carbonate, bicarbonate, chloride, bromide, iodide, and mixtures thereof.

7. A fabric treatment composition comprising the silicone polymer of Claim 3 further comprising a carrier suitable for application of the composition to fabric.

8. A hair care composition comprising the silicone polymer of Claim 3 further comprising a carrier suitable for application of the composition to the hair.

9. A method of making the silicone polymer of Claim 1 comprising the steps of:

- (a) ring-opening polymerization of an activated siloxane with a cyclic iminoether selected from the group consisting of 2-substituted-2-oxazoline, 2-substituted-5,6-dihydro-4H 1,3-oxazine, and mixtures thereof;
- (b) reduction or hydrolysis of the compound formed in step (a); and
- (c) quaternization of the compound formed in step (b).

10. The method according to Claim 9 wherein step (a) comprises a preliminary step of making the activated siloxane, the preliminary step comprising reacting a starting silicone material with an activating agent selected from the group consisting of tosyl halide, mesyl halide, and mixtures thereof;

- 5 wherein the starting silicone material has at least one hydroxy functionality terminal, the remainder terminals being non-reactive with the activating agent.

11. The method according to Claim 9 wherein the cyclic iminoether is selected from the group consisting of 2-Z'-2-oxazoline, 2-Z'-oxazine, and mixtures thereof; wherein Z' is a hydrogen, alkyl having 1 to 10 carbons, fluorocarbon having 1 to 10 carbons, phenyl, or benzyl.

12. The method according to Claim 11 wherein the cyclic iminoether is selected from the group consisting of 2-methyl-2-oxazoline, 2-ethyl-2-oxazoline, 2-propyl-2-oxazoline, and mixtures thereof.

13. The method according to Claim 9 wherein at least a stoichiometric amount to the activated siloxane of a Lewis base is used as a solvent medium at step (a).

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 97/23622

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C08G77/452 A61K7/06 D06M15/643

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A61K C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	DE 33 40 708 A (L'OREAL) 10 May 1984 see abstract see claims 1,5,6 ---	1-6,8
Y	US 4 833 225 A (D. SCHAEFER ET AL.) 23 May 1989 see abstract see column 7 - column 10, formulas ---	1-6,8
Y	PATENT ABSTRACTS OF JAPAN vol. 17, no. 462 (C-1101), 24 August 1993 & JP 05 112423 A (KAO), 7 May 1993, see abstract ---	1-6,8-13
Y	PATENT ABSTRACTS OF JAPAN vol. 98, no. 2, 30 January 1998 & JP 09 278633 A (KAO), 28 October 1997, see abstract ---	1-6,8-13
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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

### \* Special categories of cited documents :

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Date of the actual completion of the international search

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# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 97/23622

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	<p>US 4 659 777 A (J. S. RIFFLE) 21 April 1987  cited in the application  see examples 1-4  see claims 1-9  -----</p>	9-13

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International Application No

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